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NEW PERFLUOROPOLYMER-FORMING REACTIONS.(U)
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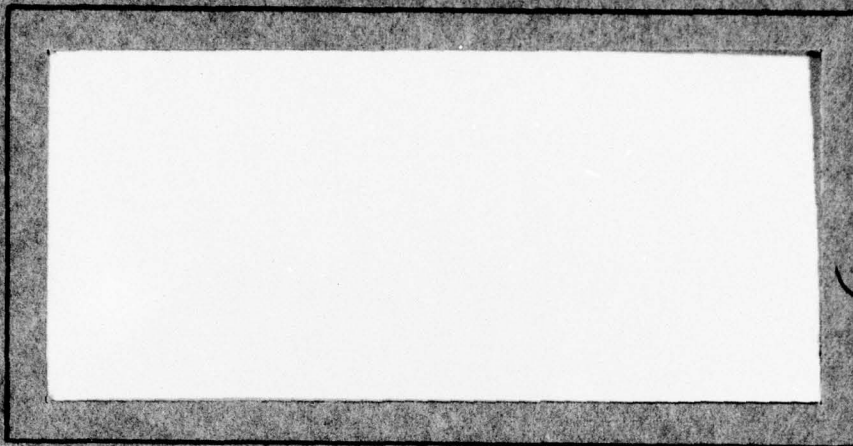
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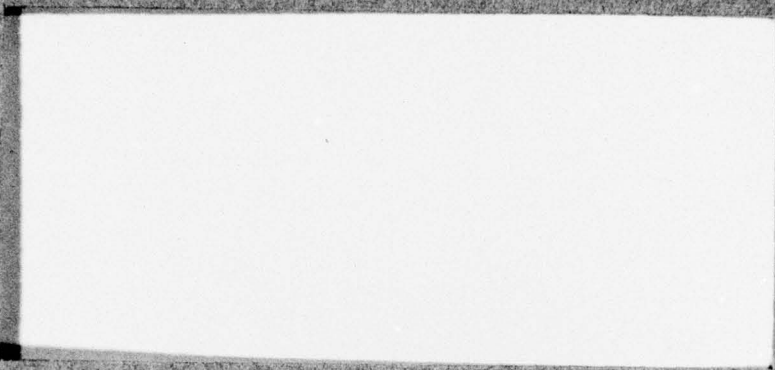
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SUMMARY

The principal lines of research activity pursued during the period of 1 March 1974 to 31 March 1979 are as follows:

- (1) Nature of oxygen-to-fluorine bond dissociations and additions,
- (2) New perfluoropolymer-forming reactions,
- (3) Synthesis of certain monomers and model compounds.

Results and details of the investigations carried out in these three areas are given in fourteen papers completed for publication. The main accomplishments are described in the report. Bibliographies of papers are included.

Collaborators, who participated in the research, were Mr. Roger S. Stringham, as the associate investigator, Dr. Donald D. Denson, who explored the synthesis of the diol $\text{HO}(\text{CF}_3)_2\text{C}(\text{CF}_2)_6\text{C}(\text{CF}_3)_2\text{OH}$, Dr. D. Thomas for mass spectra (LKB9000 and CEC21-110-B), Mr. L. Cary for ^{13}C - and ^{19}F -NMR and Mr. G.A. St. John for the field ionization mass spectra.

During the period covered by the contract, the principal investigator served on the Executive Committee of Fluorine Division of the American Chemical Society and was the recipient of a patent award from McDonnell Douglas Corporation and four certificates of recognition from NASA Invention and Contribution Board. She was invited by the National Research Council to submit an organic polymer characterization methodology outline for National Material Advisory Board Committee and became a reviewer of Polymer Program for the National Science Foundation.

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Area 1. Nature of Oxygen-to-Fluorine Bond Dissociations
and Additions

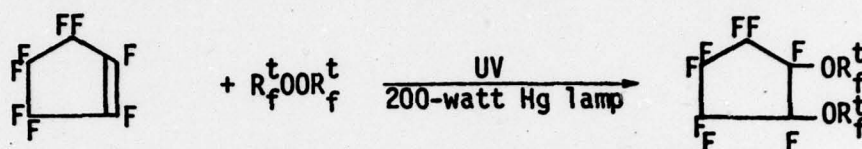
Publications:

1. "Electrophilic Additions Involving Fluoronium Ions. II. The Addition of Fluoroxy Groups to Perfluoroaromatic Compounds," M.S. Toy and R.S. Stringham, J. Fluorine Chem., 5, 31 (1975).
2. "Photochemical Reactions of Fluoroxyperfluoroalkanes with Perfluorocycloolefins," M.S. Toy and R.S. Stringham, J. Fluorine Chem., 5, 481 (1975).
3. "Photochemical Reactions of Perfluorodialkyl Peroxides with Perfluorocycloolefins," M.S. Toy and R.S. Stringham, J. Fluorine Chem., 7, 375 (1976).
4. "Addition Reaction of Tetrafluorohydrazine to Perfluoro-t-butyl Hypofluorite," M.S. Toy and R.S. Stringham, J. Fluorine Chem., 7, 229 (1976).

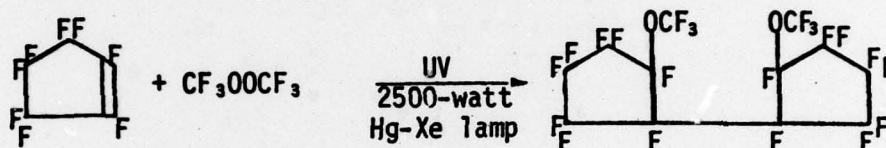
The effort was first directed toward understanding the homolysis and heterolysis of the covalent O-F bond of tertiary fluoroxyperfluoroalkane. The high electrophilicity of $(\text{CF}_3)_3\text{COF} \gg \text{CF}_3\text{OF}$ was established. Under photolysis $(\text{CF}_3)_3\text{COF}$ readily undergoes one-electron reduction in the presence of perfluorocycloolefins to yield $(\text{CF}_3)_3\text{CO-OC}(\text{CF}_3)_3$ as the major product. The formation of the peroxide confirms the homolysis of the O-F bond of $(\text{CF}_3)_3\text{COF}$ under photolysis. The dissociations of the O-F bond were also studied by reacting $(\text{CF}_3)_3\text{COF}$ with N_2F_4 in the presence and absence of photolysis. Under photolysis N_2F_4 dissociates into $\text{NF}_2\cdot$ radicals, which function as fluoroxy fluorine atom acceptors, and forms very volatile inert NF_3 by-product and the peroxide $(\text{CF}_3)_3\text{CO-OC}(\text{CF}_3)_3$. In the absence of photolysis N_2F_4 functions as a fluoronium ion acceptor and forms a white $(\text{CF}_3)_3\text{CO}^-\text{N}_2\text{F}_5^+$ salt, m.p. about 150°C . The differences of reactions and reaction products from $\text{CF}_3\text{O}\cdot$ and $(\text{CF}_3)_3\text{CO}\cdot$ radicals through the photolysis of the corresponding peroxide and perfluorocycloalkenes were studied and mechanisms discussed. The other

significant accomplishments during the course of the study are the discovery of several new synthetic methods:

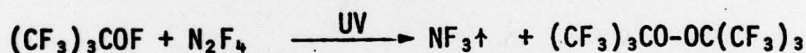
- A new vicinal perfluorodi-t-butoxyalkane synthesis e.g.,



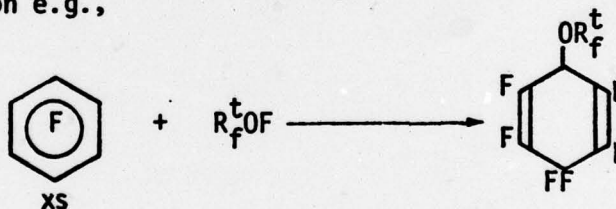
- A new 2,2'-perfluorodimethoxycycloalkyl synthesis e.g.,



- A new bis(perfluoro-t-butyl) peroxide synthesis e.g.,



- A new perfluoroether synthesis via aromatic nuclear-addition reaction e.g.,



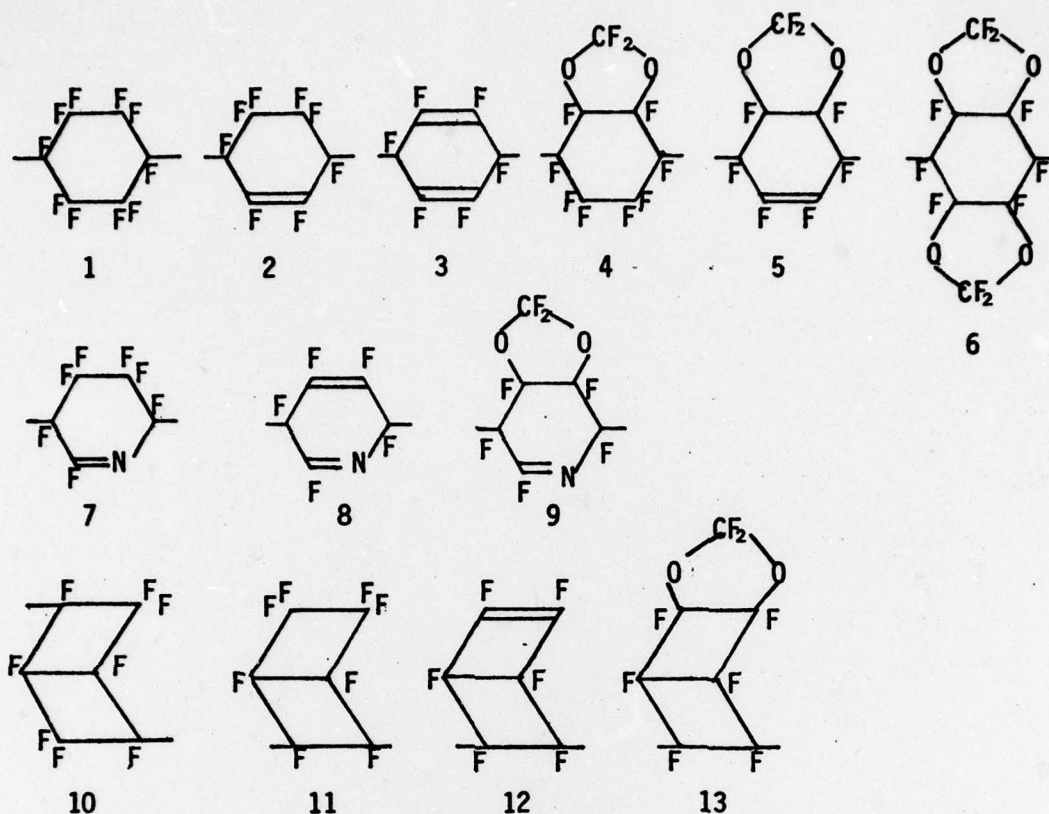
From the preparative viewpoint the last example provides a convenient method for the synthesis of many new perfluorocarbocyclic ethers, polyethers and ether-containing intermediates.

Area 2. New Perfluoropolymer-Forming Reactions

Publications:

5. "NMR Studies on Microstructures of Polyperfluorobutadiene," M.S. Toy and R.S. Stringham, J. Polymer Sci., B, 14, 717 (1976).
6. "NMR Studies of Some Perfluorocarbocyclic Ethers and Polyethers," M.S. Toy and R.S. Stringham, Am. Chem. Soc. Polymer Preprints, 18 (2), 438 (1977).
7. "Copolymerization Reactions of 'Dewar' Hexafluorobenzene," M.S. Toy and R.S. Stringham, Am. Chem. Soc. Polymer Preprints, 19 (1), 534 (1978).
8. "Fluorine-19 and Carbon-13 NMR Spectra of Polyperfluorobutadiene," M.S. Toy and R.S. Stringham, Chapter 1 in "Applications of Polymer Spectroscopy" edited by E.G. Brame, Academic Press (1978).
9. "Some Perfluorocarbocyclic Ethers and Polyethers from Hexafluorobenzene," M.S. Toy and R.S. Stringham, J. Polymer Sci., A-I, 16, 2781 (1978).
10. "Some New Perfluoroethers and Copolymers from 'Dewar' Hexafluorobenzene," M.S. Toy and R.S. Stringham, J. Fluorine Chem., 13, 23 (1979).
11. "Copolymerization of Pentafluoropyridine," M.S. Toy and R.S. Stringham, Am. Chem. Soc. Polymer Preprints, 20 (1) in press (1979); accepted to J. Polymer Sci., Part B.
12. "The Polymerization of Octafluoronaphthalene," M.S. Toy and R. S. Stringham, will be submitted to Am. Chem. Soc. Polymer Preprints, Sept., 1979.

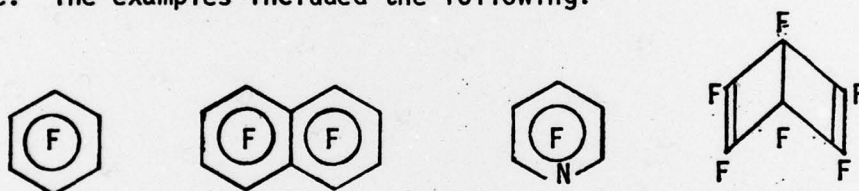
The emphasis was directed toward the addition reaction of difunctional fluoroxyperfluoroalkane with perfluoroaromatic (C_6F_6), perfluoro-N-heteroaromatic (C_5F_5N) and para-bonded perfluoroaromatic ('Dewar' C_6F_6) to form copolymers. The purpose is in interposing stable $-OCF_2O-$ linking groups between the six-membered ring-moieties. For example, the moieties 1 to 6 were obtained from C_6F_6 , moieties 7 to 9 from C_5F_5N and moieties 10 to 13 from 'Dewar' C_6F_6 .



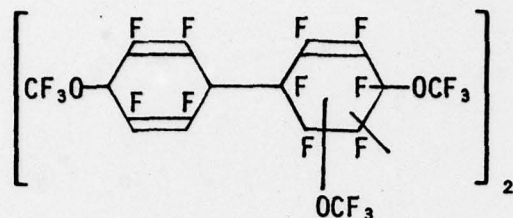
The problem of understanding and evaluating the new perfluoropolymer-forming reactions appears to have three main parts. First, there is a need to identify the volatile small molecules and to interpret their ^{19}F NMR, so that the information can aid in deducing the new perfluoropolymer microstructures. Secondly, there is the pressing need to develop microanalytical techniques in identifying these novel perfluorocarbocycles, perfluoro-N-heterocycles and perfluorobicycles and in correlating to the polymeric products. Thirdly, we need to comprehend the polymerization mechanism of the propagating species through the relationship with the volatile terminating and non-terminating products at the various stages of the polymerization process.

The homonuclear ^{19}F decoupling technique was used to help in assigning the coupling constants between the various ^{19}F nuclei in a perfluorocarbocyclic, perfluoro-N-heterocyclic or perfluorobicyclic molecule in ascertaining the isomeric or conformational structures. The ^{13}C NMR of perfluoropolymers was shown possible by probe modification of Varian XL-100 model through pulsed energy input. A gas chromatography-infrared analyzer (Perkin Elmer 567-Sadtler CIRA 101) was used not only for identification but also in separating the volatile mixtures for other instrumental analyses. Gas chromatography-mass spectrometry (LKB 9000) using 13eV was used for molecular ion determinations. The latter method, which was aided by information storage and retrievable system, provided an expedient approximation method in scanning the isomer numbers by showing the same m/e values but at different elution times.

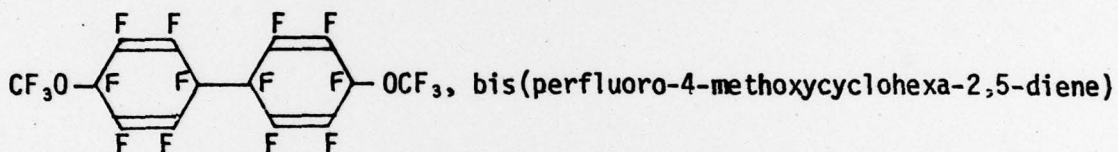
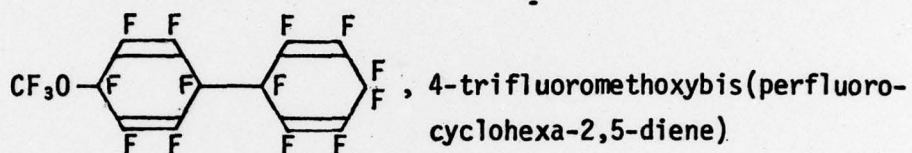
The copolymerizability of $\text{CF}_2(\text{OF})_2$ was established with perfluoroaromatic, perfluoro-N-heteroaromatic and para-bonded perfluoroaromatic. The examples included the following:



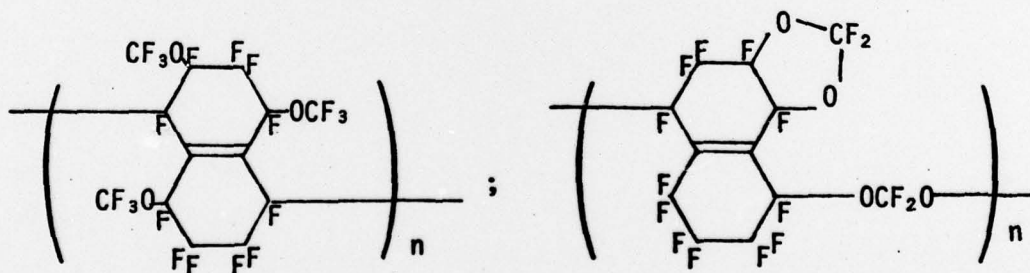
These comonomers were interposed by stable $-\text{OCF}_2\text{O}-$ linking groups, but did not form simple alternate copolymers. Fluorination and pendant perfluoro-1,3-dioxolane ring formation occurred simultaneously during copolymerization. Homopolymerizability of perfluoroaromatics was also established by CF_3OF through aromatic nuclear-addition reactions. The homopolymerization of hexafluorobenzene and octafluoronaphthalene happened concurrently with fluorination and pendant trifluoromethoxy group additions to the aromatic rings. The hexafluorobenzene oligomer of molecular weight 1254 as the major product was elucidated at follows:



in the presence of simple adduct $\text{CF}_3\text{OC}_6\text{F}_7$, perfluorocyclohexadienes, bis(perfluorocyclohexa-2,5-diene) and new isomeric perfluoroethers, e.g.,



The octafluoronaphthalene homopolymer and copolymer with increased comonomer mole ratio of C_{10}F_8 to CF_3OF or $\text{CF}_2(\text{OF})_2$ at about 1:3 gave almost quantitative glassy solids, which showed unsaturation between the carbons common to both rings, e.g.,



These solid perfluoropolyethers (m.p. $<100^{\circ}\text{C}$) were soluble in hexafluoro-benzene and perfluoro-2-butyltetrahydrofuran (FC-75). Future study on the reactivity of these olefinic bonds between the carbons common to both rings is warranted. Contribution to the basic knowledge here is anticipated in providing many breakthroughs in new materials.

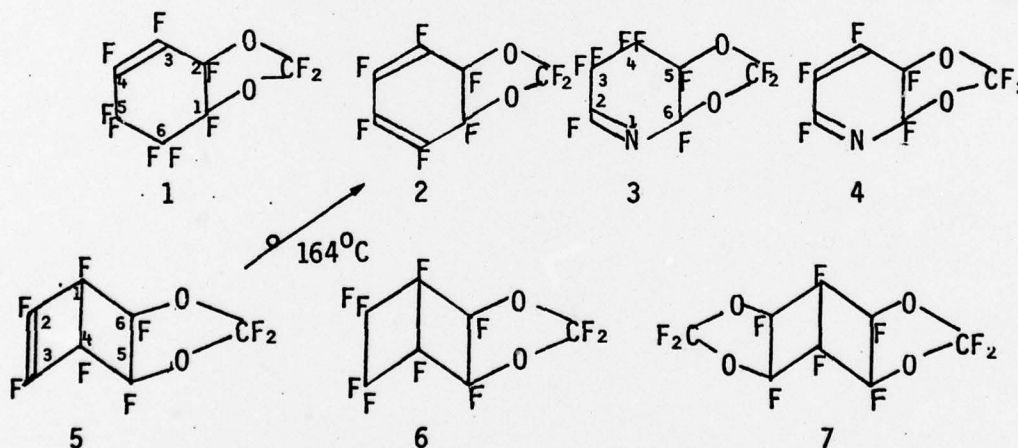
Area 3. Synthesis of Certain Monomers and Model Compounds

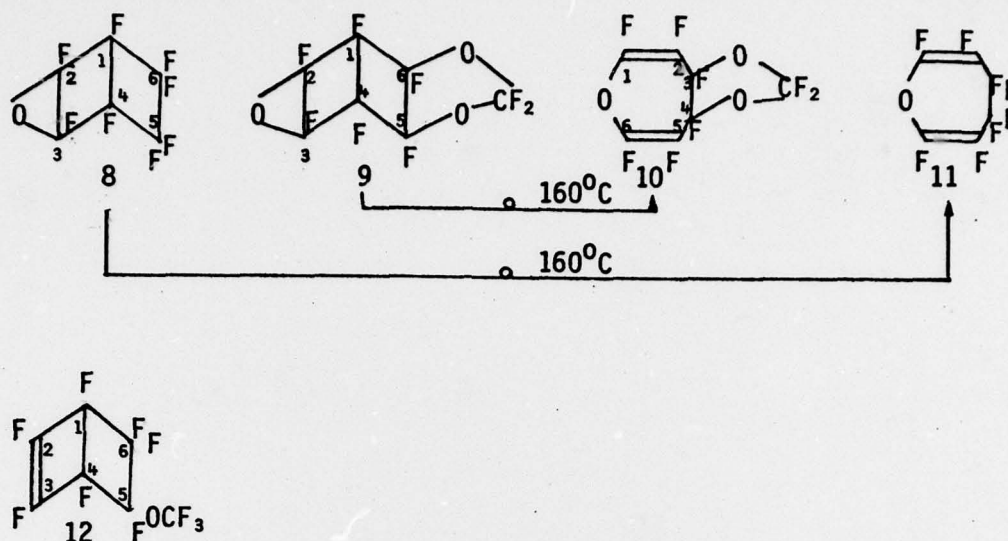
Publications:

13. "Thermal Isomerization of Perfluorobicyclo[2.2.0]hexene Oxides," M.S. Toy and R.S. Stringham, submitted to J. Org. Chem.
14. "Thermal Isomerization of a Perfluorobicyclo[2.2.0]hexene Derivative," M.S. Toy and R.S. Stringham, J. Fluorine Chem., May, 1979.

In some cases modified polymerization reaction conditions were applied in favoring the volatile fraction or certain volatile products. This was done in order to obtain specific compounds for characterization, identification and confirmation studies.

The following new perfluorocarbocyclic compounds 1 and 2 were obtained by reacting $\text{CF}_2(\text{OF})_2$ with hexafluorobenzene, compounds 5 to 11 with hexafluorobicyclo[2.2.0]hexa-2,5-diene and new perfluoro-N-heterocarbocycles 3 and 4 with pentafluoropyridine:





Compound 12, which was obtained by reacting 'Dewar' C₆F₆ with CF₃OF, homopolymerized readily to a viscous liquid through the strained olefinic bond in the presence of oxygen with low fluorine content under photolysis. The epoxidation of compound 12 was not detected.

Unimolecular isomerization happened for three compounds 5, 8 and 9 at 160 to 165°C to compounds 2, 11 and 10 respectively. Although thermal isomerization study of 12 was not carried out, a similar rearrangement such as 5 to 2 upon heating is expected, while the polymerization of 5 was not studied, but an identical strained olefinic bond polymerization as 12 is expected.

Attempts at the synthesis of the diol HO(CF₃)₂C(CF₂)₆C(CF₃)₂OH from Br(CF₂)₆Br gave low yields of the product.